

AD/A-001 344

RHEOLOGY OF CONCENTRATED SUSPENSIONS
OF SPHERES. I. EFFECT OF THE LIQUID-
SOLID INTERFACE

Sheau Van Kao, et al

Monsanto Research Corporation

Prepared for:

Office of Naval Research
Advanced Research Projects Agency

August 1974

DISTRIBUTED BY:



DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION Unclassified
Monsanto Research Corporation	2b. GROUP

3. REPORT TITLE

Rheology of Concentrated Suspensions of Spheres. I. Effect of the Liquid-Solid Interface.

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

5. AUTHOR(S) (First name, middle initial, last name)

Sheau Van Kao, Lawrence E. Nielsen, and Christopher T. Hill

6. REPORT DATE August 1974	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
8a. CONTRACT OR GRANT NO N00014-67-C-0218	9a. ORIGINATOR'S REPORT NUMBER(S) HPC 74-166	
b. PROJECT NO	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.		
d.		

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Office of Naval Research Washington, D. C.
-------------------------	---

13. ABSTRACT

A coaxial cylinder viscometer was used to measure the rheological behavior of concentrated suspensions of glass spheres in a nonpolar liquid (liquid polybutadiene), a polar liquid (glycerol), and a liquid of medium polarity. The glass beads had untreated surfaces, surfaces with absorbed octylamine, or hydrophobic surfaces prepared by treating the surfaces with dimethyldichlorosilane. All the suspensions were Newtonian, except for the suspension of silane treated beads in glycerol which was pseudoplastic. Contact angle and sedimentation measurements indicate that the glycerol-silane treated beads system contained beads in an agglomerated state. The viscosities of the suspensions obey a Mooney type equation. In the Newtonian systems all the suspensions containing treated glass surfaces had lower relative viscosities than the analogous system with untreated surfaces.

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Department of Commerce
Springfield, VA 22151

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Rheology Suspensions Viscosity Sedimentation Contact angle Interface						

RHEOLOGY OF CONCENTRATED SUSPENSIONS OF SPHERES

I. EFFECT OF THE LIQUID-SOLID INTERFACE

BY

Sheau Van Kao,
Lawrence E. Nielsen
and
Christopher T. Hill

Materials Research Laboratory
Washington University
St. Louis, Missouri 63130

August 1974

D D O

DEC 2 1974

19

Monsanto/Washington University Association
High Performance Composites Program
Sponsored by ONR and ARPA
Contract No. N00014-67-C-0218, ARPA Order 876

Approved for Public Release: Distribution Unlimited

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies either expressed or implied, of the Advanced Research Projects Agency or the U. S. Government.

11

FOREWORD

The research reported herein was conducted by the staff of Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 87, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites".

The prime contractor is Monsanto Research Corporation. The Program Manager is Dr. Rolf Buchdahl (Phone 314-694-4721).

The contract is funded for \$7,000,000 and expires 30 June, 1974.

Rheology of Concentrated Suspensions of Spheres

I. Effect of the Liquid-Solid Interface

Sheau Van Kao, Lawrence E. Nielsen
and Christopher T. Hill
Materials Research Laboratory
Washington University
St. Louis, Missouri 63130

Abstract

A coaxial cylinder viscometer was used to measure the rheological behavior of concentrated suspensions of glass spheres in a nonpolar liquid (liquid polybutadiene), a polar liquid (glycerol), and a liquid of medium polarity. The glass beads had untreated surfaces, surfaces with adsorbed octylamine, or hydrophobic surfaces prepared by treating the surfaces with dimethyldichlorosilane. All the suspensions were Newtonian, except for the suspension of silane treated beads in glycerol which was pseudoplastic. Contact angle and sedimentation measurements indicate that the glycerol-silane treated beads system contained beads in an agglomerated state. The viscosities of the suspensions obey a Mooney type equation. In the Newtonian systems all the suspensions containing treated glass surfaces had lower relative viscosities than the analogous systems with untreated surfaces.

Rheology of Concentrated Suspensions of Spheres

I. Effect of the Liquid-Solid Interface

Introduction

Over a hundred papers have been published on the rheology of suspensions of spheres (1). At low concentrations of rigid spheres, the suspensions are Newtonian in behavior and agree with the Einstein prediction (2). At high concentrations, the theories are inadequate to explain the experimental results. Experimentally it is found at high concentrations that the suspensions may be either Newtonian or non-Newtonian, and two suspensions of the same concentration may behave entirely differently (3). These differences, for the most part, are related to the extent of particle agglomeration, which in turn is related to the nature of the liquid-solid interface. It was the objective of this work to study the effect of the liquid-solid interface on the rheology by systematically changing the chemical nature of the liquid and the surface of the spherical particles.

Materials and Methods

Glass beads of the size 1-30 microns were used for this study. These beads, soda-lime type, were obtained from Cataphote Co. (Jackson, Miss.). Microscopic examinations showed these particles to be highly regular and perfect spheres. The iron powder which is normally found in small size glass beads was carefully removed with a magnetic rod. Afterwards, the beads were cleaned in refluxing isopropanol and vacuum dried at 150°C for several days to remove possible adsorbed water. The surface treatments of glass beads were conducted in liquid media at room temperature. For the silane coupling agent, dimethyldichlorosilane (GE SC 3002), beads were first stirred

in carbon tetrachloride, then the agent was introduced into the slurry. For the surface active agent, octylamine, methyl alcohol was the medium. After adding the treating agents, the slurries were further stirred for two hours. Then the beads were washed several times with fresh liquid and dried in a vacuum oven.

Three Newtonian liquids of different nature were used as dispersing media. The first one, glycerol, is a polar liquid with a viscosity of 920 c.p. and a density of 1.26 g/cc at 25°C. The second one, Thanol SF-6500 (Jefferson Chemical Co.) is a urethane grade polyol of 6500 molecular weight containing three hydroxyl groups per molecule with a viscosity of 1310 c.p. and a density of 1.02 g/cc (at 25°C). This is a medium polar liquid. The third liquid is a low molecular weight resin (molecular weight = 2000-3000), Lithene PH (Lithium Co. of America). Chemically, it is a mixture of cis and trans polybutadiene. The resin is an amber-colored nonpolar liquid. The viscosity of Lithene is 2300 c.p. and its density is 0.897 g/cc at 25°C.

Suspensions of particles with different surface treatments in different liquids were prepared by introducing the liquid into a flask containing the glass beads under vacuum. Mixing was then conducted under vacuum for several hours. Viscosity measurements were made immediately upon the cessation of mixing to minimize possible error caused by sedimentation.

A rotational concentric cylinder viscometer, Rotovisco (Haake Instruments), was used to measure the rheological behavior of suspensions. The separation of the inner cylinder and the outer cylinder is 2.75 mm. The outer cylinder is stationary, while the inner cylinder can rotate with 30 different speeds ranging from

0.036 rpm to 583.2 rpm. The shear stress on the inner cylinder can be read directly from the instrument. The true shear rates were calculated using the method suggested by Krieger and Maron (4). All the measurements were taken under a constant temperature of 25°C.

Sedimentation velocity and volume of suspension were measured in a graduated cylinder. The height of the boundary line between the suspension and the clear liquid left above was recorded as a function of time. The initial sedimentation velocity and the maximum packing volume fraction, ϕ_m , can be obtained from these experiments.

Contact angles were obtained by measuring a sessile drop through a telescope. Since it is not possible to measure the contact angle on glass beads, glass slides were used which were surface treated at the same time as the glass beads.

Results and Discussion

Some of the flow curves are shown in Figs. 1-6. Calculated relative viscosities are in Table I. Sedimentation data are shown in Figs. 7 and 8 and in Table II. Contact angles are listed in Table III. Bingham yield stresses for the nonwetting system, dimethyldichlorosilane treated beads in glycerol, are shown in Fig. 9. For the sake of clarity, many curves have been omitted from these figures, and some of the experimental points have been omitted from the curves.

Up to volume concentrations of 40 percent, all the systems are Newtonian except beads treated with dimethyldichlorosilane suspended in glycerol. This system has a Bingham (5) yield stress which increases nearly linearly with rate of shear so that an apparent or Bingham viscosity may be calculated from the slope of the curves. The viscosity of all the systems can be represented by the Mooney equation (6). The

Einstein coefficient varies between 2.50 and 2.88 for the Newtonian systems, but the apparent Einstein coefficient for the Bingham system is 2.27. The maximum packing fractions calculated for the Mooney equation vary between 0.74 and 0.85. These empirical values are greater than the values determined from sedimentation measurements, which generally gave packing volumes less than 0.60 as listed in Table II.

Contact angle measurements indicate that all the liquids wet the clean glass surface and glass containing adsorbed octylamine. The non-polar and medium polar liquids poorly wet the glass treated with dimethyldichlorosilane. Polar glycerol does not wet the glass treated with the silane (contact angle greater than 90°). Liquids which wet a solid particle should produce good dispersions without agglomerates since the liquid can force its way between particles which are in contact and force them apart. Particles which are not wetted by a liquid are expected to form agglomerates when a suspension is made.

Sedimentation measurements substantiate the conclusion that the silane treated beads are agglomerated in glycerol while the other systems are not agglomerated. The unagglomerated systems settle rapidly to a low sedimentation or packing volume. The agglomerated silane beads in glycerol either settle more rapidly to a large sedimentation volume, or these suspensions develop such a high yield stress that they do not settle at all.

Agglomeration results in dramatic changes in the flow behavior by converting the Newtonian flow curves to flow curves which have a yield point. Silane treated beads in glycerol was the only system studied which showed a yield point. Theory indicates that the yield

stress should increase as the square of the concentration (7). Fig. 9 does indicate an approximate dependence upon the square of the volume fraction of beads. At first glance, the agglomerated systems appear to have definite Bingham yield stresses. However, at very low shear rates some data points in Figs. 5 and 6 show that the stresses drop down toward the origin. Other experiments, using a modified Stormer viscometer, were made to measure the yield stresses directly. No true yield stress was found in these experiments carried out at very low rates of shear. Therefore, it is concluded that the flow behavior of the agglomerated suspensions is pseudoplastic rather than truly plastic.

Suspensions containing the nonpolar polybutadiene liquid and the medium polar Thanol liquid do show a difference between untreated beads and beads which have been treated with either octylamine or silane. The treated beads consistently give a lower relative viscosity than the untreated ones. However, there do not appear to be any consistent trends in either the contact angle measurements or the maximum packing fractions which can explain the viscosity results. Other experiments (to be reported in another paper (7)) indicate that traces of water may profoundly modify the flow behavior of suspensions. Probably the relatively small differences found between treated and untreated beads in nonpolar or medium polarity liquids are due to traces of water on the untreated glass bead surfaces.

Conclusions

The nature of the liquid-solid interface can have a large effect on the rheology of concentrated suspensions. Treatments which produce

low energy surfaces can reduce the relative viscosity of Newtonian systems as long as the liquids wet the surface so that gross agglomeration does not occur. Highly polar liquids which do not wet low energy surfaces produce suspensions in which the particles are highly agglomerated. The agglomerated systems are pseudoplastic in their rheological behavior, and they show apparent yield stresses.

Acknowledgment

The work described in this paper is a part of the research conducted by the Monsanto/Washington University Association sponsored by the Advanced Research Projects Agency, Department of Defense, under Office of Naval Research contract N00014-67-C-0218, formerly N00014-66-C-0045.

References

1. Rutgers, I. R., *Rheologica Acta*, 2, 305 (1962).
2. Einstein, A., *Ann. Phys.*, 4, 19 (1906); *ibid.*, 34, 591 (1911).
3. Landel, R. F., Moser, B. G., and Bauman, A. J., "Proc. 4th Internat. Congr. Rheology", Part 2, p. 663, Interscience, New York, 1965.
4. Krieger, I. M. and Maron, S. H., *J. Appl. Phys.*, 24, 134 (1953).
5. Bingham, E. C., *J. Phys. Chem.*, 29, 1201 (1925).
6. Mooney, M., *J. Colloid Sci.*, 6, 162 (1951).
7. Kao, S. V., Nielsen, L. E., and Hill, C. T., Monsanto/Washington University Association, HPC 74-167 and HPC 74-168, August 1974.

Table I
Relative Viscosities of Suspensions

Liquid	Volume Fraction of Beads	Relative Viscosity		
		Untreated Beads	Octylamine Treated	Silane Treated
Glycerol	0.150	1.671		1.463*
	0.200	1.967	2.03	1.957*
	0.250	2.609		2.391*
	0.300	3.391	3.48	3.087*
	0.350	5.124		4.022*
	0.400	8.152	9.35	5.858*
Thanol	0.150	1.702		1.618
	0.200	2.104	2.01	1.966
	0.250	2.695		2.503
	0.300	4.110	3.66	3.473
	0.350	5.788		4.874
	0.400	9.591	9.02	7.507
Lithene (Polybutadiene)	0.150	1.687		1.638
	0.200	2.153	2.10	2.012
	0.250	2.769		2.594
	0.300	3.830	3.70	3.543
	0.350	5.354		4.899
	0.400	9.591	9.17	7.874

* Using Bingham plastic viscosity.

Table II
Maximum Packing Volume Concentrations of Suspensions

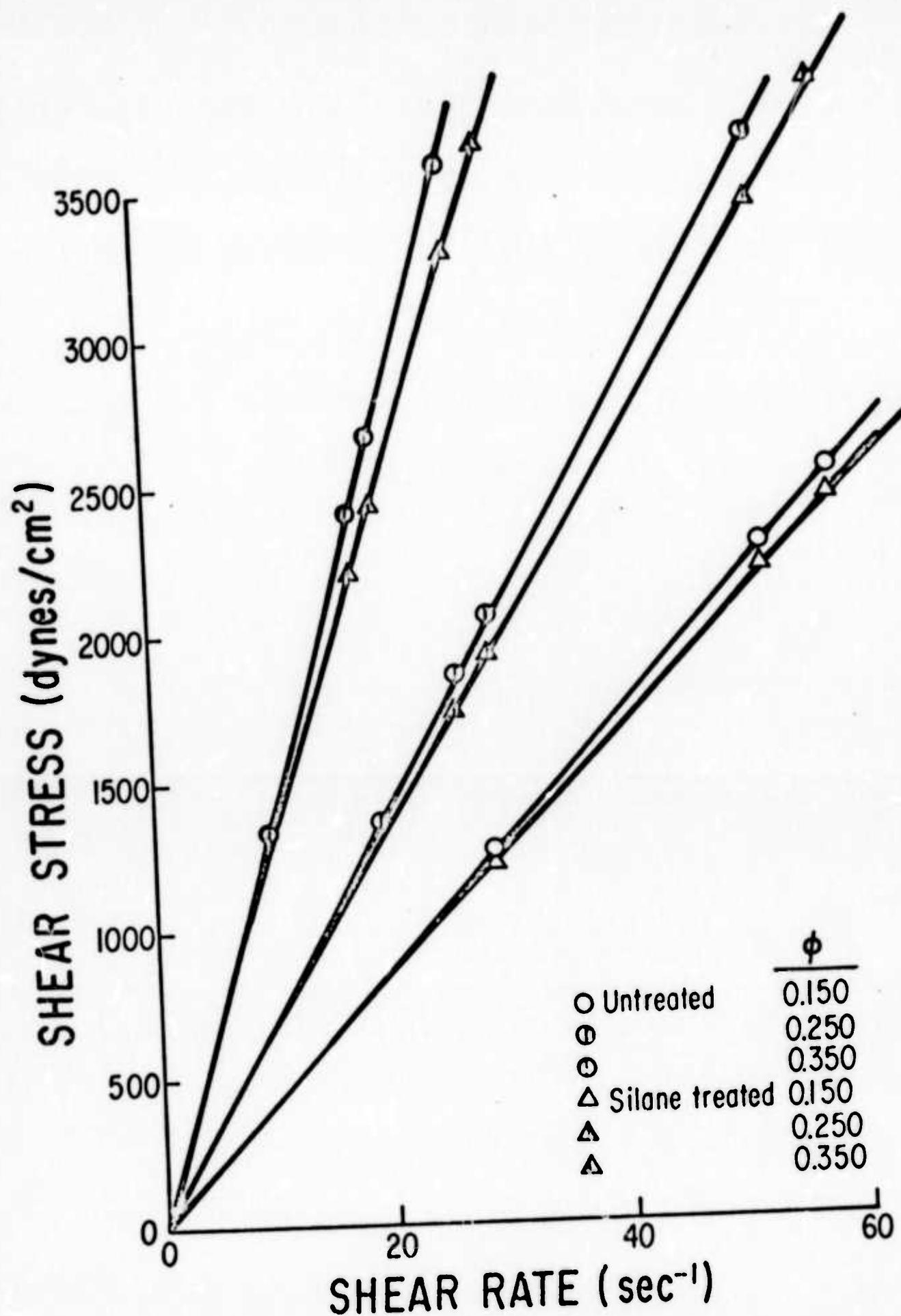
System	Volume Fraction of Spheres	Maximum Packing Fraction ϕ_m
Untreated Beads - Glycerol	0.15	0.58
" " "	0.25	0.58
" " "	0.35	0.58
" " "	0.55	0.62
Untreated Beads - Thanol	0.15	0.53
" " "	0.25	0.55
" " "	0.35	0.57
" " "	0.60	0.60
Untreated Beads - Polybutadiene	0.15	0.56
" " "	0.25	0.58
" " "	0.35	0.60
" " "	0.50	0.60
Silane Treated - Glycerol	0.15	0.24
" " "	0.25	0.26
" " "	0.35	0.36
Silane Treated - Thanol	0.15	0.54
" " "	0.25	0.56
" " "	0.35	0.57
" " "	0.55	0.59
Silane Treated - Polybutadiene	0.15	0.55
" " "	0.25	0.56
" " "	0.35	0.56
" " "	0.50	0.59
" " "	0.55	0.61

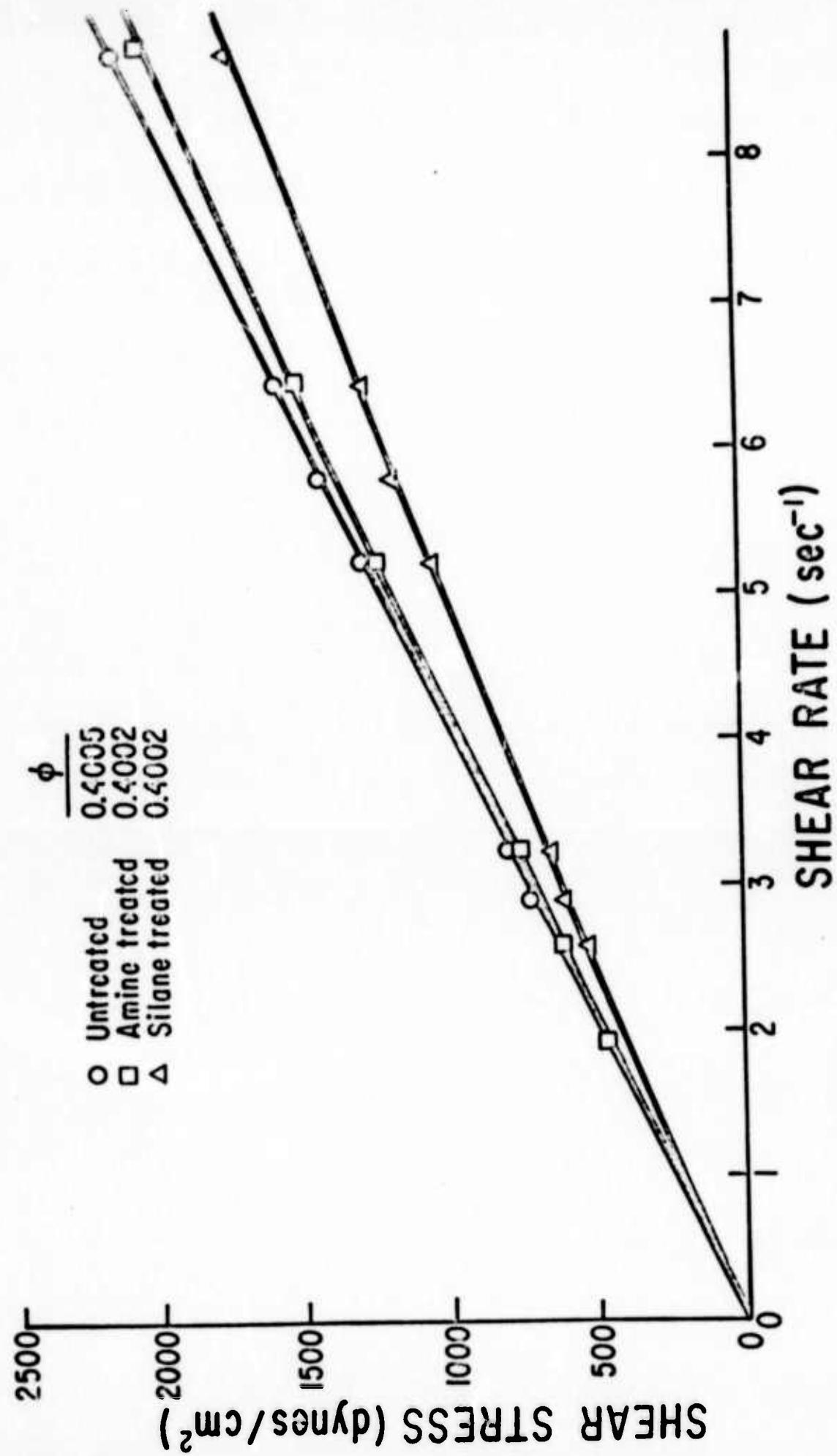
Table III
Contact Angles of Liquids on Different Surfaces

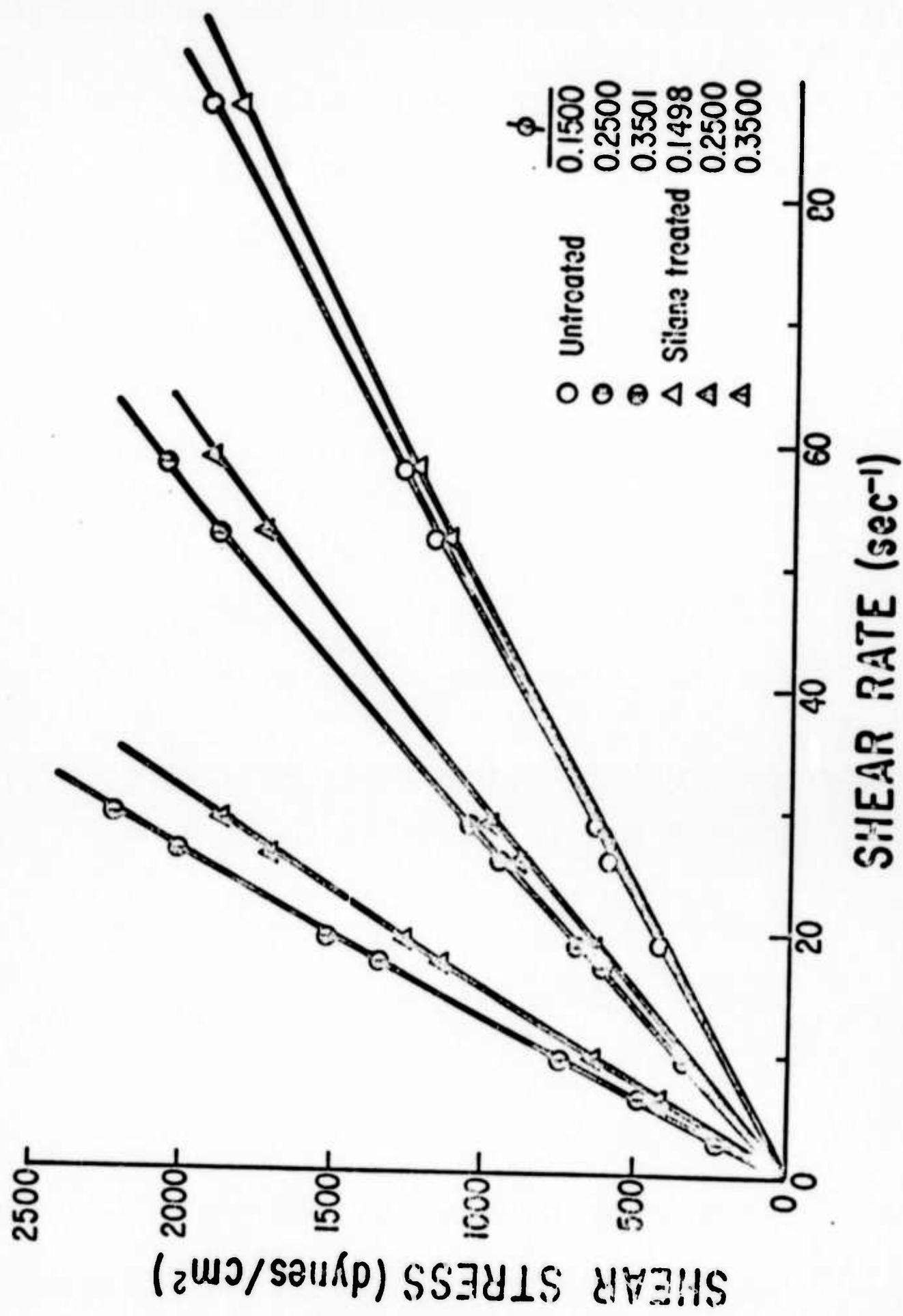
Liquid	Surface Treatment		
	Clean Glass	Dimethyldichlorosilane	Octylamine
Water	< 14°	94°	38°
Glycerol	19°	93°	36°
Thanol	22°	60°	< 7°
Lithene PH (Polybutadiene)	17°	64°	12°

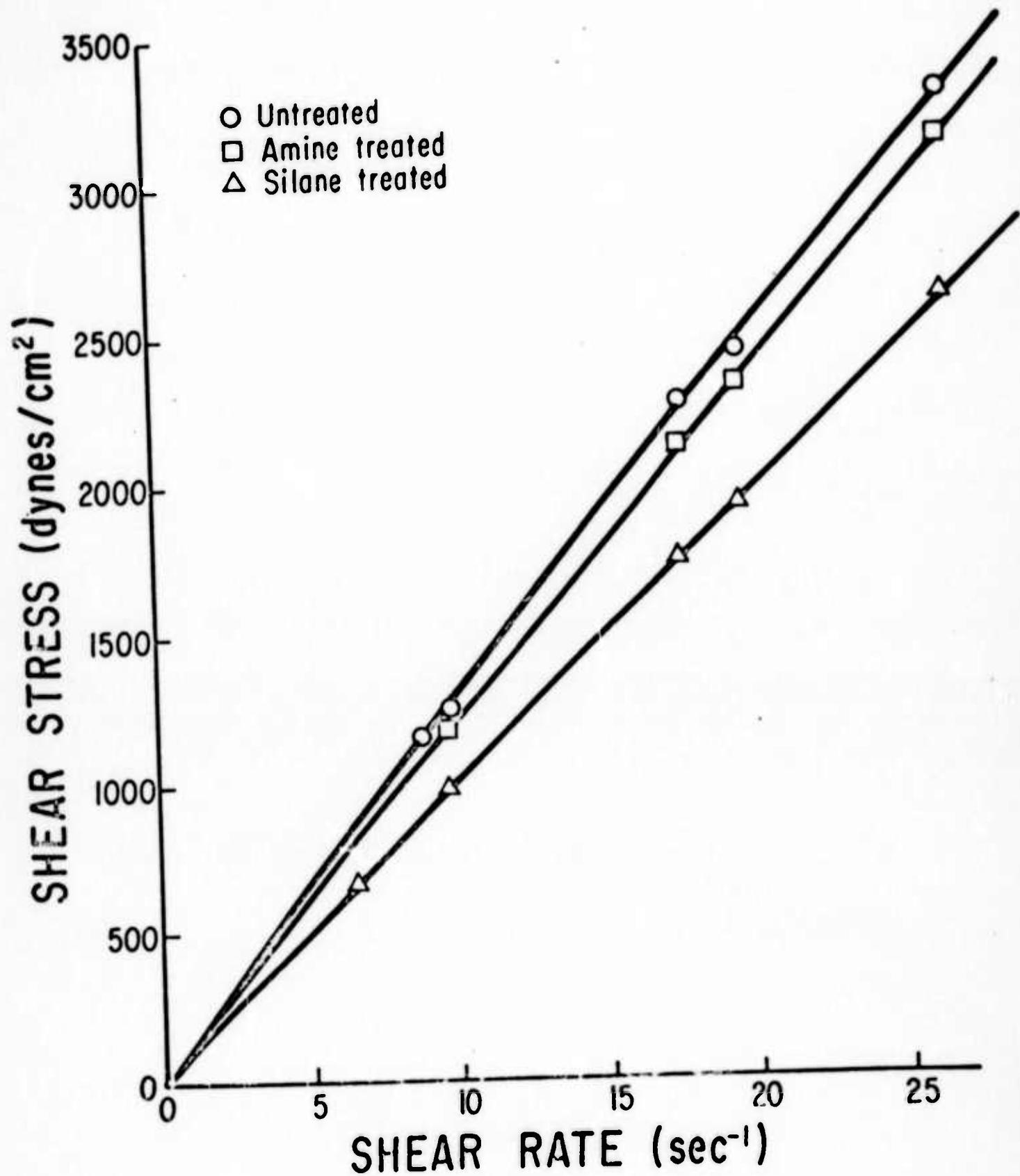
Figures

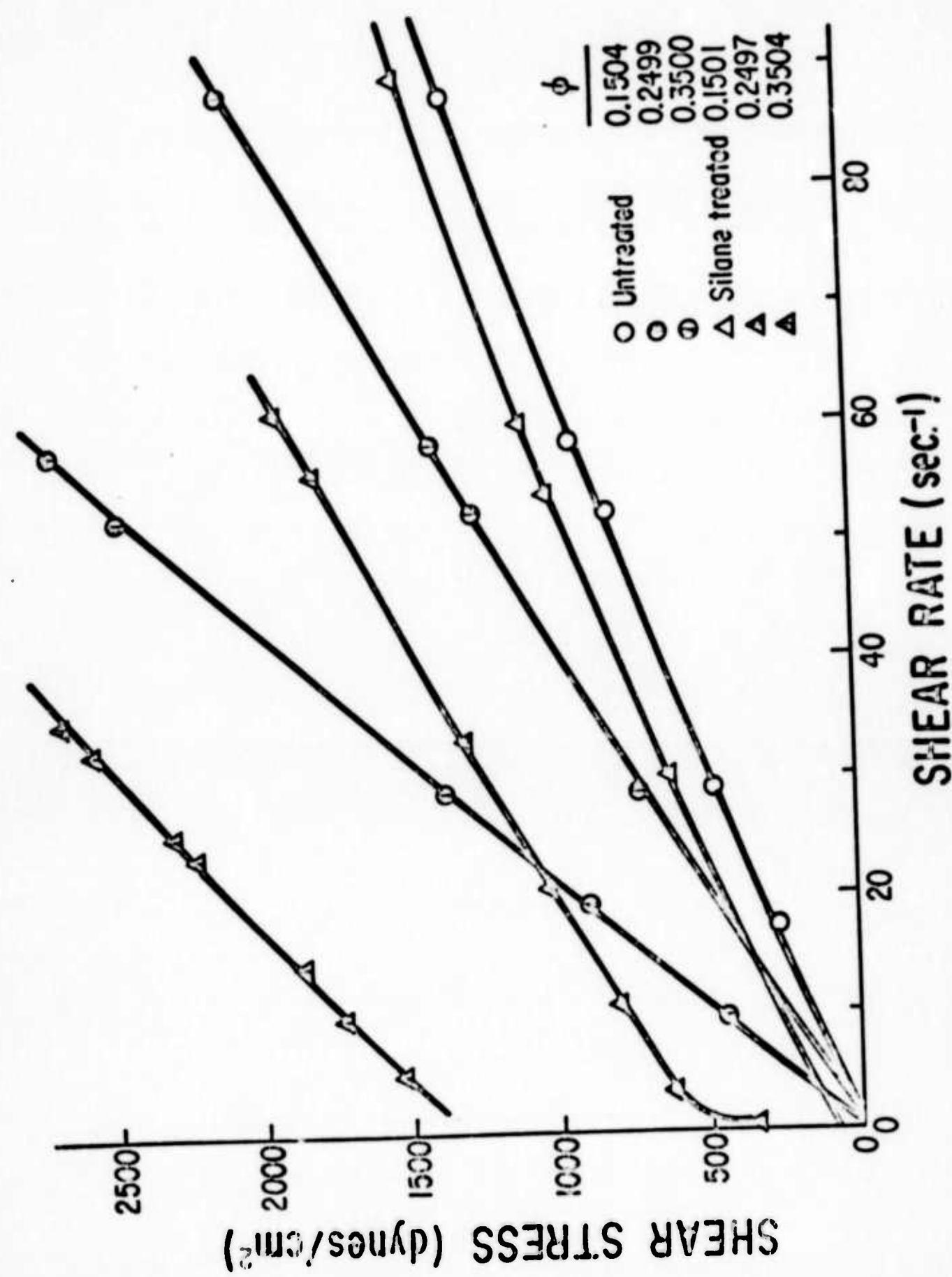
1. Flow curves of suspensions of glass beads in liquid polybutadiene (Lithene). ϕ = volume fraction of beads.
2. Effect of surface treatments on the flow curves of suspensions of glass beads in liquid polybutadiene. Volume fraction of beads is 0.400.
3. Flow curves of suspensions of glass beads in Thanol liquid. ϕ = volume fraction of beads.
4. Effect of surface treatments on the flow curves of suspensions of glass beads in Thanol liquid. Volume fraction of beads is 0.400.
5. Flow curves of suspensions of glass beads in glycerol.
6. Effect of surface treatment on the flow curves of suspension of glass beads in glycerol. Volume fraction of beads is 0.400.
○ Untreated, □ Amine treated, △ Silane treated.
7. Sedimentation curves of suspensions of glass beads in Thanol liquid. Volume fraction of beads is 0.150.
8. Sedimentation curves of suspensions of glass beads in glycerol.
9. Bingham yield stresses of suspensions of dimethyldichlorosilane treated glass beads in glycerol.

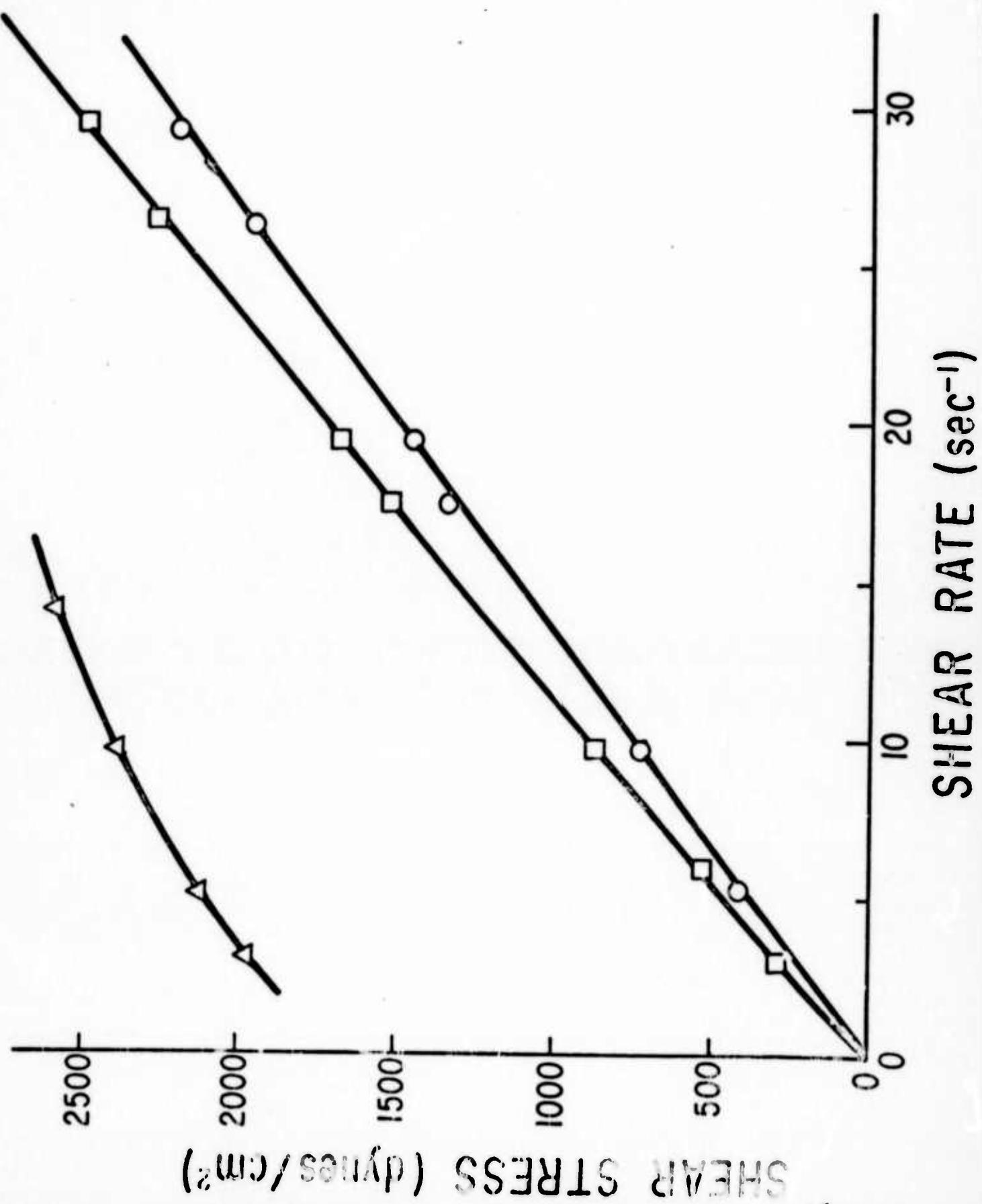


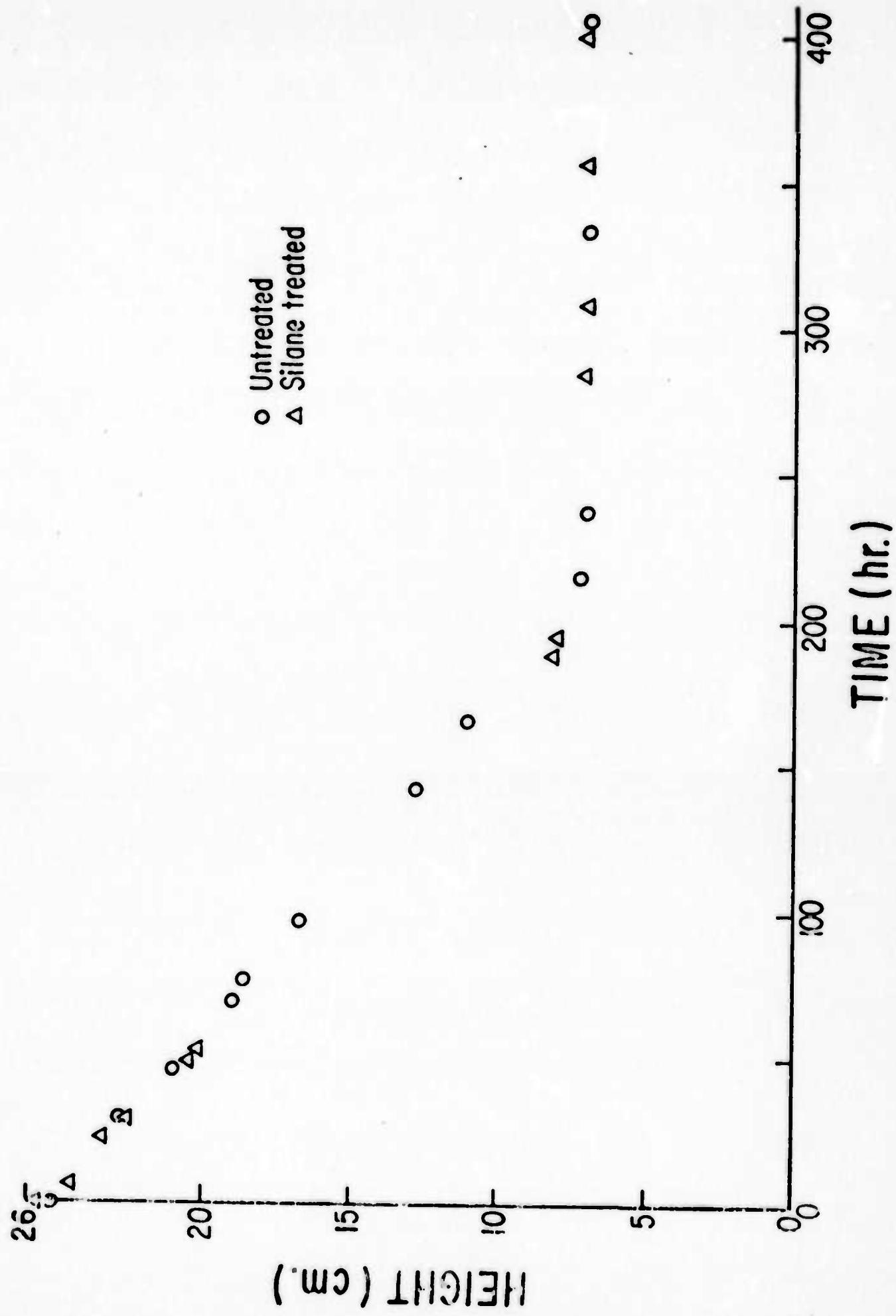


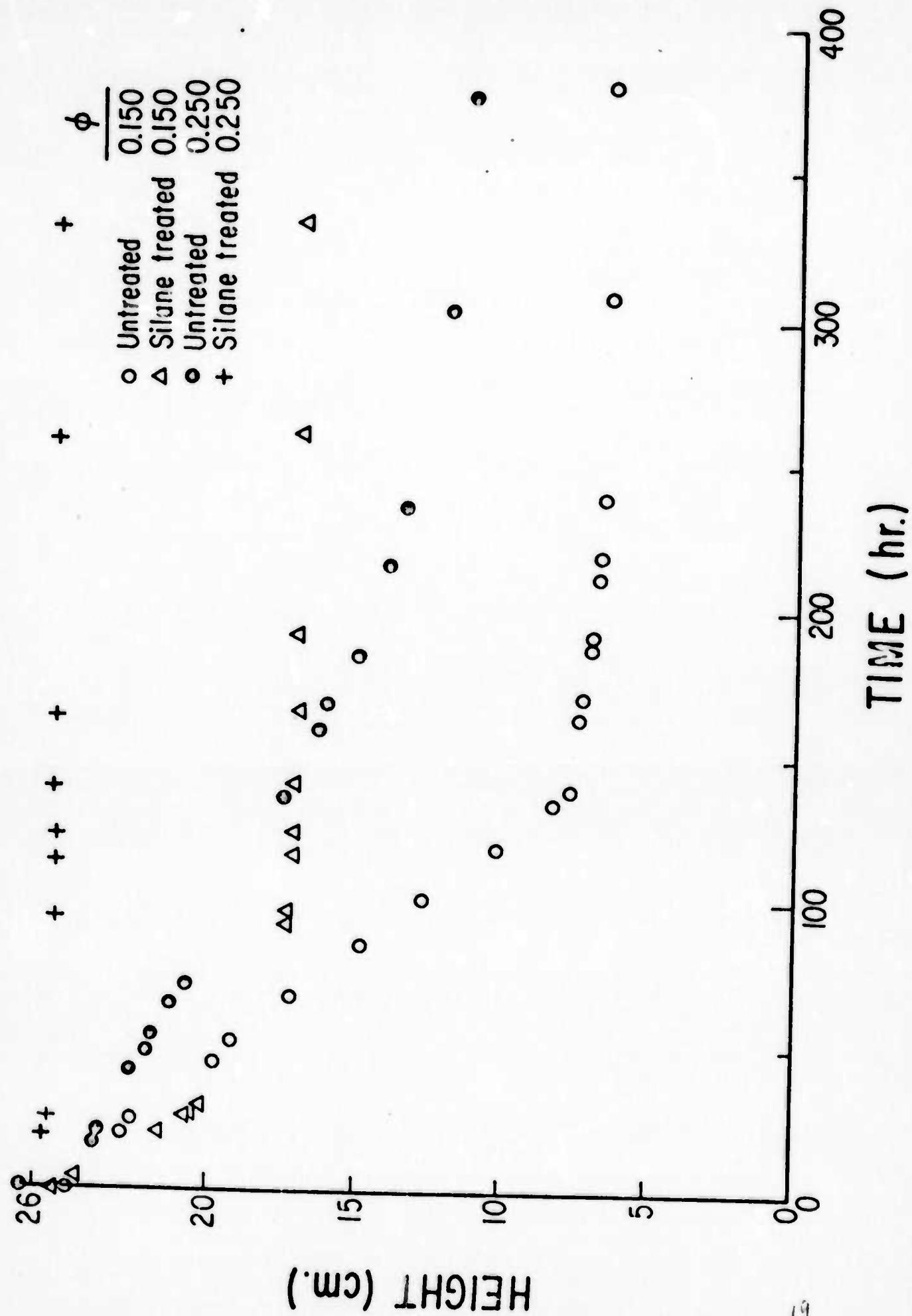












SHEAR STRESS (dynes/cm²)



ϕ^2